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THE COMPARATIVE INFLUENCE OF SHORT AND LONG RANGE ELECTRIC FIELDS IN THE SALTS OF THE IRON GROUP OF ELEMENTS. PART III.

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ABSTRACT. In Part II of the present paper it was found that several instances of the existence of the effect of the long range fields, in paramagnetic salts of the first half of the iron group of elements, arose, in spite of the conditions there being unfavourable for such observations. In the second half of the iron group the removal of orbital degeneracy by the cubic field in the first approximation, is less perfect. In consequence, Jahn-Teller distortions of the whole crystal lattice occur, giving rise to deviations from cubic field and hence further removal of the orbital degeneracy and to some extent the spin degeneracy. The spin-orbit coupling restores some of the orbital moment and at the same time causes a restraint on the orientations of the spins. These also lead to Jahn-Teller repercussions throughout the crystal lattice and to the final stabilization of the Stark-energy levels. It is thus seen that the final stabilization of the energy in the paramagnetic salts is dependent on the long range fields, especially when removal of orbital degeneracy by the cubic field is imperfect. Clear evidence of this is found from the salts of the ions Fe^{++}, Co^{++}, and to a smaller extent of Ni^{++}. Evidence from Cu^{++} salts is inconclusive for various reasons.

1 INTRODUCTION

In the previous part of this paper (Bose and Mitra, 1952) we found a small but appreciable effect of the changes in the crystalline electric fields, on the magnetic behaviour of the ions of the first half of the iron group, arising from the changes of the ions and dipoles lying outside the immediate neighbours of the paramagnetic ion. It was discussed there that the Jahn-Teller conditions of stability for a paramagnetic ionic cluster, when extended to the entire crystal lattice may be enough to explain the removal of the degeneracy of both the spin and the orbital states of the paramagnetic ion.

In the second half of the iron group the orbital contributions to the magnetic moments are in general large, even when the lowest cubic state in the Stark-pattern of an ion is non-degenerate, and we expect here a correspondingly larger deviation of the moments from salt to salt and from solid to solution, containing the same paramagnetic ion.

DISCUSSIONS

The exprimental data are much more extensive and reliable in the latter half of the iron group than the first. But here again the variations of

the results from author to author make it extremely difficult to compare the absolute magnitudes of the actions of the long and short range fields. We take up, as before, the results represented in the form of graphs of the square of mean effective moments against the absolute temperatures (figures 1-7)*.

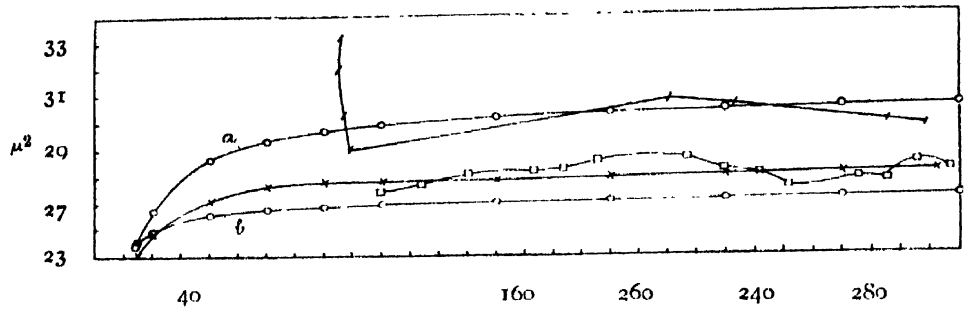

FIG. 1

μ^2 versus T curves for Fe^{++} salts.

1. ⊙ - - - Jackson.—(*a*) $Fe(NH_4SO_4)_2.6H_2O$; (*b*) $FeSO_4.7H_2O$
2. × - - - Onnes and Oosterhuis—$FeSO_4\ 7H_2O$
2. □ - - - Ishiwara—$FeSO_4\ 7H_2O$
4. | - - - Foex—$Fe(NH_4SO_4)_2.6H_2O$.

(1) *Fe^{++} salts.* From the fact that an orbital triplet T_2, lies lowest in the Stark-pattern of the octahedrally coordinated salts of Fe^{++} ion we should expect large orbital Jahn-Teller distortions of both the long and the short range structures in such salts (Bose and Mitra, 1952). Thus, in the two salts studied, namely, $FeSO_4.7H_2O$ and $Fe(NH_4,SO_4)_2.6H_2O$ in both of which Fe^{++} ions are surrounded by an octahedron of 6 water molecules, the differences observed in the temperature variation curves of the moments (figure 1) must be due to differences in the long range fields alone, On an examination of the curves, we can immediately discard Ishiwara's (1915) and Foex's (1921) measurements as being wholly unreliable. Then, even admitting rather large differences in Jackson's (1924) and Onne's (1924) curves for $FeSO_4.7H_2O$ as being due to systematic errors in calibration or tendency for oxidation of the salt, it will be seen that a fairly large difference exists between the curves of the above two salts. It is known from the X-ray structures of the two salts (Hofmann (1931) ; Beevers and Schwartz (1935)) that the crystals of the two salts, though both monoclinic, are not in the same space group, the single salt belonging to C_{2h}^6 with 16 molecules in the unit cell and the Tutton salts to C_{2h}^5 with two molecules. Of the two salts, the former evidently has a lesser *internal* symmetry and it is therefore very satisfactory that it actually shows a larger quenching of the effective moment. It is further interesting to note that at low temperatures the curve for $FeSO_4.7H_2O$ is less steep than that for the Tutton salt, showing lesser influence of the spin quenchings as also of the higher order field terms in this region. Represen-

* For full references please see Part I of the present paper (Bose and Mitra)

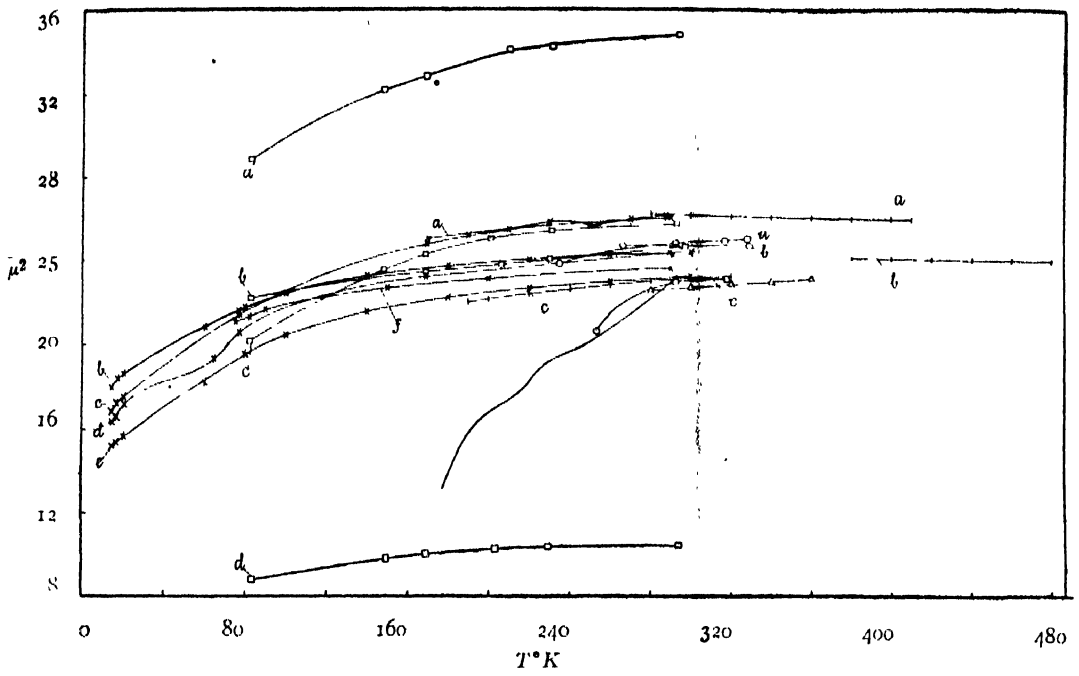

FIG. 2

μ^2 versus T curves for Co^{++}salts

Bartlett - - - ⊙
- *a*. $Co(KSO_4)_2.6H_2O$
- *b*. $Co(NH_4SO_4)_2.6H_2O$
- *c*. $CoSO_4.7H_2O$

2 Janes - - □
- *a*. $CoSO_4.6NH_3$
- *b*. $K_2Co(SCN)_4.4H_2O$
- *c*. $CoCl_2.6NH_3$
- *d*. $Co(CN)_2.2H_2O$

3. Jackson - - - ×
- *a*. $Co(KSO_4)_26H_2O$
- *b*. $CoSO_4\ 7H_2O$
- *c*. $Co(RbSO_4)_2.6H_2O$
- *d* $Co(KSO_4)_2.6H_2O$
- *e*. $Co(NH_4SO_4)_2.6H_2O$
- *f* $CoSO_4.7H_2O$

. Chatillon - - |
- *a*. $CoCl_2.H_2O$
- *b*. $CoCl_2.6H_2O$ molten blue
- *c*. $CoCl_2.6H_3O$ solid.

5. Serres - - Δ
$CoSO_4.7H_2O$

6. Mercier .. –
$CoCl_2$ soln in methanol.

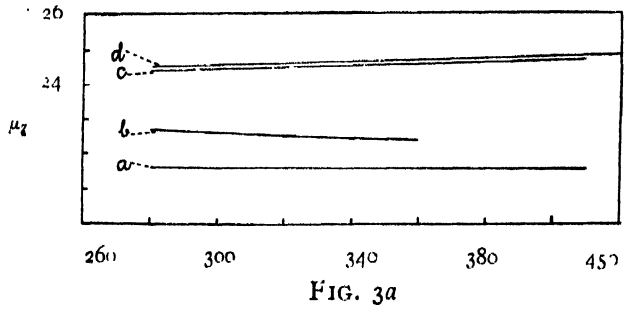

FIG. 3*a*

μ^2 versus T curves for solutions of Co^{++} salts.

Author – Chatillon—*a*. $CoCl_2$ soln in amyl alcohol.
- *b*. $CoCl_2$ soln. in ethyl alcohol:
- *c*. $(CoNO_3)_2$ aq. soln.
- *d*. $CoCl_2$ and $CoSO_4$ aq. soln.

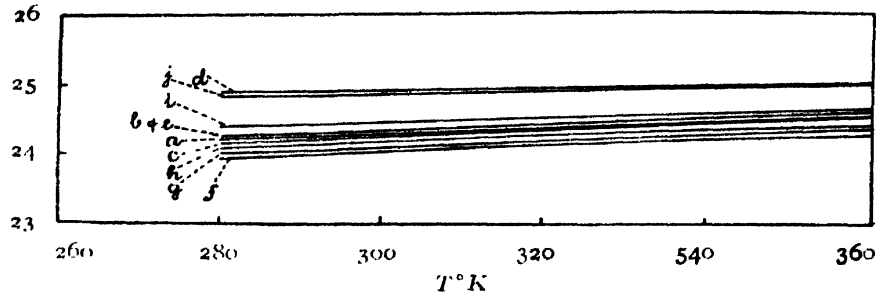

FIG. 3*b*

Author—Lallemand—$CoCl_2$ aq. soln, conc. in gms. per gm. soln.

Indep. of Conc.

1. $a = .041 : b = .0207 : c = .091 :$

Dependent on conc. & mode of preparation

2. $d = .017 : e = .325 : f = .072 : g = .046 :$
$h = .031 : i = .022 : j = .0125.$

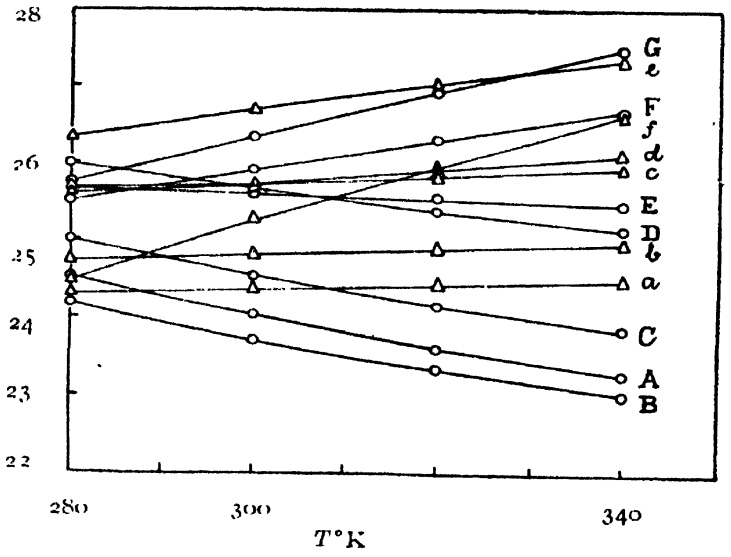

FIG. 4

μ^2 versus T curves for solutions of Co^{++} salts.

Author—Wahlenbrach.

$CoCl_2.6H_2O$ aq soln.

A = 7.382 conc. gms./100 c.c. soln.
B = 4.434
C = 2.957
D = 1.477
E = .743
F = .236
G = .118

$CoCl_2$ anhyd. aq soln

a = 2.636 conc. gms./100 cc. soln
b = 1.757 ,,
c = 1.054 ,,
d = .527 ,,
e = .264 ,,
f = .132 ,,

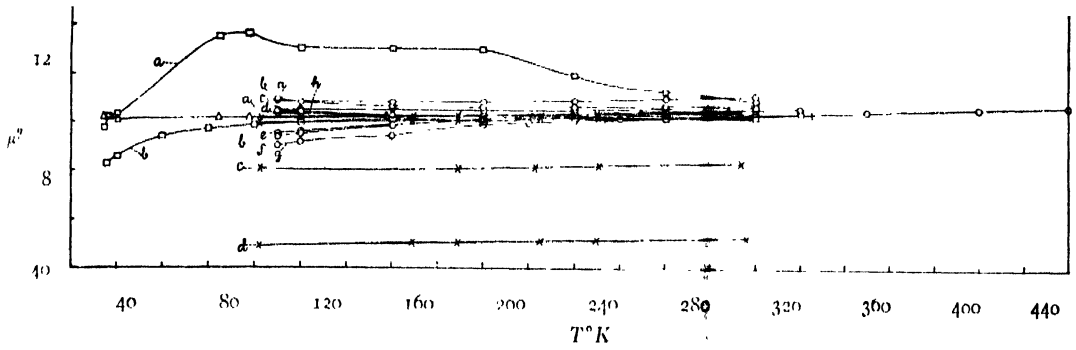

FIG. 5

μ^2 versus T curves for Ni^{++} salts.

Serres - - - O

a. $NiSO_4.8.5H_2O$: *b*. $Ni(NH_4SO_4)_2.6H_2O$: *c*. $NiSO_4.4H_2O$: *d*. $NiSO_4.6H_2O$;
e. $NiCl_2.6H_2O$: *f*. $NiSO_4.1.13H_2O$ *g* $NiSO_4.H_2O$ *h*. $NiSO_4.7H_2O$.

Jackson - - □—*a*. $NiSO_4.7H_2O$: *b*. $Ni(NH_4SO_4)_2.6H_2O$.

de Haas and Gorter .. Δ — $NiSO_4.7H_2O$

Janes - - - ×—*a*. $Ni(NO_3)_2.6H_2O$; *b*. $NiSO_4.6H_2O$; *c*. $Ni(NO)_2.4NH_3$; *d*, $Ni(CN)_2C_6H_6NH_3$

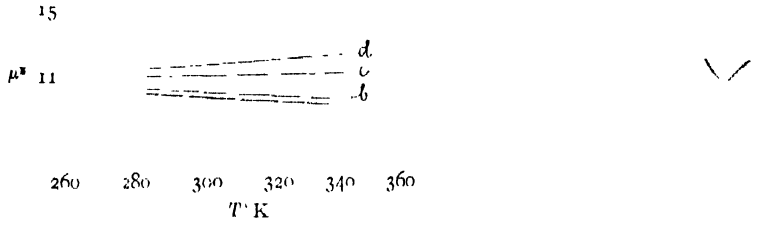

FIG. 6

μ^2 versus T curves for solutions of Ni^{++} salts.

Author—Fahlenbrach. $NiCl_2$ Solution

1. After aging , independent of conc.
   a = 7.310, 3.412, 1.707, .5845 gms. per 120 cc. soln.
2. Freshly prepared; dependent on conc.
   b = 4.271 c = 1.073 d = 0.429

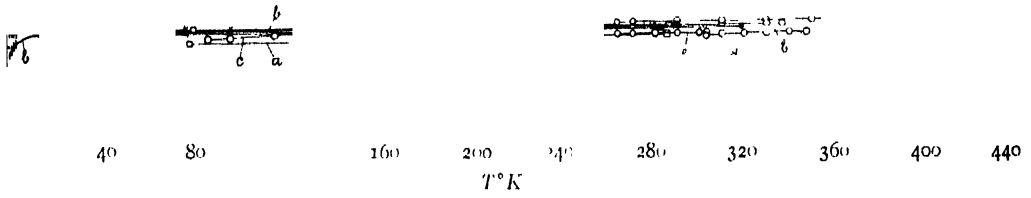

FIG. 7

μ^2 versus T curves for Cu^{++} salts and their solutions.

1. ⊙ - - - Birch—*a*. $CuSO_4.5H_2O$, *b* $CuCl_2.2H_2O$, *c*. $CuSO_4.H_2O$; *d*. $CuCl_2$ soln.; *e*. $CuCl_2$ soln.
2. O - - - Bartlett—$Cu(KSO_4)_2.6H_2O$ and $Cu(NH_4SO_4)_2.6H_2O$.
3. Δ - - - de Haas and Gorter—$CuSO_4.5H_2O$.
4. × - - - Hupse—$Cu(KSO_4)_2.6H_2O$.
5. □ - - - Janes—*a*. $CuSO_4.4NH_3.H_2O$; *b*. $Cu(KSO_4)_2.6H_2O$ & $Cu(NH_4SO_4)_2.6H_2O$.
6. ⊦ - - - Reckie—*a*. $Cu(KSO_4)_2.6H_2O$; *b*. $CuSO_4.5H_2O$.

ting the curves by a three constant formula of the type, $\overline{\mu^2}_{eff} - 24 = A + BT + \frac{C}{T}$, as we did in the previous part of the paper (*l.c.*) we find for the constants the following values (Table I). The differences in the A terms are

TABLE I

Author	Salt	A	B	C
Ornes and Oosterhuis	$FeSO_4\,7H_2O$	+4.57	−.091	−51.4
Jackson	$FeSO_4\,7H_2O$	+3.21	0	−25.6
Do	$Fe(NH_4SO_4)_2 6H_2O$	+0.23	+.0017	−66.

mostly due to differences in the short range fields, induced by differences in long range fields. The differences in the C terms which are well pronounced should be especially noted, as these come mostly from the differences in long range asymmetric fields, acting on both orbital and spin degeneracies, becoming more prominent at low temperatures. Unfortunately, no temperature variation data on solutions of Fe^{++} salts are available from which we could estimate the full action of the long range fields in these salts.

(7) Co^{++}. In the Stark-pattern of the octahedrally coordinated red Co^{++} salts an orbitally degenerate triplet Γ_4, lies lowest and hence their behaviours should not be very much different from the similarly constituted Fe^{++} salts. It has been, however, found that the case is complicated by the tendency of many Co^{++} salts to form a blue complex with a tetrahedral coordination, in the Stark-pattern of which a singlet Γ_2 lies lowest so that the behaviour approaches that of octahedrally coordinated Cr^{+++} or Ni^{++} salts. Especially, in the state of solutions the two types of complexes may be concurrently present, their relative amounts depending on temperature, concentration, mode of preparation, previous treatment, etc., so that the interpretation of the results is not easy. Corresponding to the large orbital contributions to the moment in the red salts of Co^{++} ion and also to a high degree of restraint on the spins through spin-orbit coupling and the rhombic fields, we should expect a large Jahn-Teller effect upon both short range and long range clusters. (Bose and Mitra Part II)

Let us take the graphical representations of the moments of the solid salts first (figure 2) and for obvious reasons only such as do not depend on the mode of preparations or previous history. Of the salts studied, the best for comparison would be the isomorphous monoclinic Tutton salts in which X-ray data give an octahedron of water molecules immediately surrounding each Co^{++} ion, the difference in the distant atoms being only due to the different alkali ions, *e.g.* K^+, NH_4^+ or Rb^+. The interatomic distances increase from salt to salt in the sequence of increasing ionic radius of the alkali ions. The

water octahedron has a pseudo-tetragonal symmetry and the distant atoms have monoclinic symmetry about the Co^{++} ion. Unfortunately, the magnetic data on the moments vary considerably even for the same salt done twice by the same observer,—vide the graphs for the potassium salt, also those for monoclinic $CoSO_4.7H_2O$ by Jackson (1923, 1924, 1927 1933). It is also rather disquieting that the graph of the ammonium salt by the same author should show the highest quenching of the effective moment. Much significance, however cannot be attached to these as also to the inflexions in the curve of the potassium salt nearabout 80°K, which are not confirmed by the other observations. Bartlett's (1932) curves for the same two Tutton salts are not very different from each other and actually cross. The importance of these data is, however, dubious owing to the very small range of temperature used.

In $CoSO_4.7H_2O$, which is isomorphous with $FeSO_4.7H_2O$, the Co^{++} ion is surrounded by a water octahedron but the actual internal symmetries of the atoms both near and distant are less than the Tutton salts. The data by Jackson (*l.c.*), Serres (1932) and Bartlett (*l.c.*) differ much from one another. On the whole, however, comparing all these salts one has to admit that without laying too much stress on the sequence of the changes from salt to salt, there exist fairly large differences in the moment curves of the salts, least quenching being for the rubidium salt and the highest perhaps for the heptahydrated sulphate, as it should be, in view of the increasing asymmetry of internal structure along the series.

The clustering immediately round Co^{++} ion in the hexahydrated chloride is exactly as in the previous salts but the presence of Cl^- ions marks the difference in distant atoms, of which the exact arrangements are not known, causing a larger quenching of the moment than most of the Tutton salts, as shown by Mlle. Serres' data (*l.c.*).

$CoCl_2,6NH_3$ done by Janes (1935), in which Co^{++} is surrounded by an octahedral cluster of NH_3 instead of H_2O as in the previous salts, shows a much smaller quenching effect of the NH_3 molecules compared to H_2O, the case being similar to the rubidium Tutton salt. We might have expected the salt $CoSO_4.6NH_3$ by the same author to behave not very differently. But the tremendous difference actually observed leads us to suspect that the magnetic behaviour of these ammines may be highly sensitive to changes in the long range fields. Much higher moment in the amminosulphate is evidently due to an incomplete splitting of the ground Γ_4 triplet in the Stark-pattern, the electric field on the Co^{++} ion being uniaxial ; and an inversion in Γ_4 triplet occurring owing to a comparable magitude of the 2nd and the 4th order rhombic fields, causing the doubly degenerate component of Γ_4 to lie lowest here, instead of the singlet as is probably the case in the amminochloride or the other Co^{++} salts (*vide* V^{+4} and V^{+3} salts, Bose and Mitra Part II ; Van Vleck 1939).

On the other hand, $Co(CN)_2.6H_2O$ (Janes, *l.c.*) shows an abnormally low moment much below even the spin only value of 15, no doubt owing to strong covalency common in all cyanides and this abnormality therefore is more the action of the near than the distant atoms.

$CoCl_2.H_2O$ done by Chatillon (1927) at high temperatures shows much higher moment than the hexahydrated chloride, which can only be explained as an effect of ferromagnetic spin couplings of similar ions, very likely to occur in view of its low magnetic dilution.

$CoCl_2.6H_2O$ studied in the molten state (Chatillon, *l.c.*, figure 2) is somewhat complicated by the formation of a tetrahedral phase, but clearly shows the sudden rise in the moment as the lattice breaks down at the melting point and the long range fields vanish. The cobalt salts in aqueous solutions done by Lallemand (1935) and Chatillon (*l.c*) (figures 3*a* and 3*b*) also show similar behaviour, though the same tendency for tetrahedral cluster formation mars the possibility of observing to the best advantage, the result of vanishing long range fields in these solutions. By the way, the enormous variations of the moments with concentration and temperature, of some cobalt salts observed by Fahlenbrach (1932 ; figure 2) can possibly be ascribed to such uncertain changes in the coordination of the Co^{++} ions. In the alcoholic solutions (figure 3) of the cobalt salts (1932) the effect of the above tetrahedral clustering is even more clearly marked. The case of methanol solution of $CoCl_2$ (Mercier, 1935 ; figure 2) is, however, unlike anything else and the field here must be such as to cause an even heavier quenching of the spins at low temperatures than in the cyanide.

The causes of the deviations from the Curie law can be compared in the different salts by trying to fit the curves with a three constant formula :

$$\mu_{eff}^2 = 15 - A + BT + \frac{C}{T}.$$

The values of the constants for the different salts are tabulated below, some of the results for the solid salts and the solutions having been omitted as having been measured over a too restricted range of temperatures to serve much useful purpose.

Two of Jackson's results below, marked by query, might be explained as being due to the observer having picked up for measurement, as luck would have it, some different crystal modification of the correspondin · salt, having quite different crystal field. But it would be better to repeat these results before coming to any conclusion. The other values on the same salts by Jackson were done at Leiden over a wider range of temperatures and are more reliable.

On a perusal of the rest of the table we can immediately divide it into two sets of similar results, leaving aside the solitary case of the dihydrated cyanide. The first set consists of the heptahydrated sulphate and the Tutton salts, all having comparatively small A values, indicating small

TABLE II

	Salt	Author	A	B	C
1.	$CoSO_4\ 7H_2O$	Jackson	+9.00	+.0016	−224. (?)
2.	-do-	-do-	+6.81	+.0091	−59.1
3.	$Co(KSO_4)_2.6H_2O$	-do-	+5.20	+.0117	−60.6
4.	-do-	-do-	+17.9	−.0113	−100.7 (?)
5.	$Co(NH_4SO)_2.6H_2O$	-do-	+5.06	+.0115	−74.7
6.	$Co(RbSO_4)_2\ 6H_2O$	-do-	+6.02	+.0185	−65.8
7.	$CoSO_4\ 7H_2O$	Serres	+5.77	+.0069	—
8.	$CoCl_2\ 6H_2O$	Chatillon	+9.71	+.001	−54.0
9.	$CoCl_2\ H_2O$	-do-	+11.8	−.0018	—
10.	$CoSO_4\ 6NH_3$	Janes	+20.8	+.0039	−59.7
11.	$CoCl_2\ 6NH_3$	-do-	+13.7	−.0015	−69.0
12	$K_2Co(SCN)_4\ 4H_2O$	-do-	+7.46	+.0085	−77.8
13.	$Co(CN)_2.2H_2O$	-do-	−4.19	+.0005	−178.

spin-orbit contribution from the upper cubic levels. The C values are also comparatively smaller, pointing to a small exchange of population amongst the rhombic levels and only moderate restraint on the spins, through the spin orbit coupling in these salts. The values of the constants A, B, C change from salt to salt and though the variation is not systematic the general tendency is for the values to increase in magnitude towards the rubidium salt. This is in the right direction, comparing the internal symmetries of the sulphate and the double sulphates.

The salt $K_2Co(SCN)_4.4H_2O$ (Janes, l. c.) appears to have the contributions from A, B and C terms not much different from the previous salts, the small difference seeming to indicate a crystalline field splitting of lesser magnitude in this salt.

The other set of salts comprising the chlorides, hexammines have a much higher numerical values of the constants A, B, and C, which is possible only if as already mentioned crystalline fields are smaller and more symmetric causing a large contributions from upper cubic levels, from the rhombic levels of the lowest Γ_4 triplet as also large spin quenchings through spin-orbit coupling and the rhombic field. The order of decreasing strength of the of fields is evidently along the series $CoCl_2\ 6H_2O$, $CoCl_2\ H_2O$, $CoCl_2.6NH_3$ and $CoSO_4.6NH_3$. However, as was mentioned previously in connection with the ammino-sulphate, it now appears probable that in all these cobalt salts the lowest triplet is only partially separated into a doublet and singlet by a (nearly) uniaxial field existing in these crystals and the 2nd and the 4th order rhombic fields are in such a ratio as to cause an inversion of the rhombic triplet Γ_4 in passing from 1st set of salts to the 2nd set, so that the singlet is lowest in the first and the doublet in the 2nd This strengthens our former belief that the cobalt salts are very sensitive to even small changes in the long and the short range electric fields and provides us with a nice example of the Jahn-Teller distortional effects of the long range fields.

That the spin quenchings are of the 1st order in $Co(CN)_2.2H_2O$ is shown clearly by the -ve value of the temperature independent term A, and the variations of the orbital contributions are also large as shown by the C term.

(3) Ni^{++}. In the octahedrally coordinated salts of Ni^{++} ion, just like Cr^{+++} ion, the $^1A_1$ nondegenerate state lies lowest in the Starkpattern. But the spin-orbit coupling in Ni^{++} ion is -335 cm^{-1}, as against +87 cm^{-1} in Cr^{+++}. Also in Ni^{++} ion with 8 electrons as against 3 in Cr^{+++}, there is no Kramer's spin degeneracy. Hence the spin-orbit contributions from the upper cubic levels as also spin quenchings will be much larger. Evidently the effect of the long range fields should be more pronounced in the Ni^{++} salts. The results of the measurments on the Ni^{++} salts are plotted in graphs of μ_{eff}^2 against T(Fig). Excepting a few, e.g., the salt $NiSO_4.7H_2O$ by Jackson (l.c.) which are known to be in error, and the salts $Ni(NO_2).4NH_3$ and $Ni(CN)_2C_6H_6NH_3$ by Janes (l.c.), which must have strong covalent fields acting in them, the rest only of the salts approximately obey the Curie Law, with squares of the moments differing appreciably from the spin only value of 8, as are to be expected. The percentage deviations of the moments from salt to salt are somewhat larger than in Cr^{+++} salts (vide Part II). Further, the slopes of the curves are markedly different at low temperatures.

A three constant formula $\overline{\mu_{eff}^2} - 8 = A + BT + \frac{C}{T^2}$, applied to these curves yields the values of the coefficients A, B and C as tabulated below.

TABLE III

	Salt	Author	A	B	C
1.	$NiSO_4.H_2O$	Serres	+2.28	+.0017	−130.
2.	$NiSO_4.1\,13H_2O$	do	+1.68	+.0038	−61.2
3.	$NiSO_4.4H_2O$ 300°-140°K	do	+1.21	+.0034	+108.
	do 140°-90°K	do	+1.79	+.0038	+25.2
4.	$NiSO_4.6H_2O$	do	+1.25	+.0035	+62.2
5.	$NiSO_4.7H_2O$	do	+1.17	+.0033	+77.7
6.	$NiSO_4.8.5H_2O$	do	+1.36	+.0034	+107.
7.	$Ni(NH_4SO_4)_2.6H_2O$	do	+1.62	+.0041	+72.9
8.	$NiCl_2\,6H_2O$	do	+1.79	+.0025	−48.5
9.	$NiSO_4\,6H_2O$	Janes	+1.79	+.0014	—
10.	$Ni(NO_3)_2\,6H_2O$	do	+1.93	+.0017	—
11.	$Ni(NO_2)\,4NH_3$	do	−5.45	+.0023	−23.3
12.	$Ni(CN)_2C_6H_6.NH_3$	do	−3.14	+.0012	+6.04
13.	$NiSO_4\,7H_2O$	de Haas & Gorter	+1.82	+.0022	+4.45
14.	do	Jackson	+8.99(?)	−.0193	−102. (?)
15.	$Ni(NH_4SO_4)_2\,6H_2O$	do	+2.20	+.0002	−31.4 (?)

The largest number of salts studied, are by Mlle Serres (1933) but unfortunately the structures in most cases are not known. Even, in the hexhydrated and heptahydrated sulphates and the ammonium Tutton salt, where structures are known, the salts are not isomorphous so that it is difficult to compare the

action of the distant atoms. In these three salts and the hexhydrated chloride the Ni^{++} ions are all surrounded by 6 water molecules. The heptahydrated sulphate, being the most asymmetric structure of these should have the smallest value of the coefficient A and next in order should come, the Tutton salt, the hexahydrated chloride and then the hexahydrated sulphate. Excepting the value for the last, which appears to be rather too small, the other salts fall in a right sequence. It may be noticed that Janes' measurements for the hexahydrated sulphate and nitrate place them approximately in their correct position in the sequence. The large discrepancies in the values of the constants in the salts $NiSO_4.H_2O$ and $NiSO_4.1.13H_2O$ cannot be easily explained though it is note worthy that the compositions of the salts are rather uncertain and the coordinations unstable. Further, exchange interactions are of importance in such magnetically concentrated salts.

The negative value of the C terms in the above two salts as also in $NiCl_2.6H_2O$ should be noted indicating a total quenching of the moments below liquid hydrogen temperatures. The high +ve values of C for most of the other salts done by Serres may not have much significance in view of the fact that for the salt $NiSO_4.7H_2O$ Serres' value for C is +77.7, as against the value of +4.45 by Gorter and de Haas, (Leid. Comm) done with great care over a wider range of temperatures, though the absolute value of the moment may not be as accurate as that of Serres $NiSO_4.4H_2O$ is interesting in that its crystalline fields above 140°K, resembling $NiSO_4.6H_2O$ and $NiSO_4.8,5H_2O$ are very much modified below 140°K, approaching the behaviour of $NiSO_4.7H_2O$ of Gorter and de Haas and of $NiCl_2.6H_2O$ of Serres, indicating very different internal symmetries above and below 140°K.

It is of course possible that differences in the signs and magnitudes of the C terms in different salts might be partly due to exchange effects and partly of the changes in the action of the distant atoms to which the rhomic field constants are highly sensitive. It is noteworthy that in the field theory of Penny and Schlapp (1932) they have taken into account only the A and B terms in the mean moment of Ni^{++}, C term being accurately zero. But they have not considered the action of the distance atoms in this theory which may have quite important contributions to the C term.

The two complex salts done by Janes (*l c.*) are definitely strongly covalent as is shown by the strong quenching of the moments. The values of A, B, C for $Ni(NH_4SO_4)_2.6H_2O$ by Jackson (*l.c.*) are quite different from Serres' and incompatible with the previous accounts.

As regards the measurements on solutions at different temperatures the only data are by Fahlenbrach (*l.c.*; figure 6) giving wide variations of the moment, with concentration and temperature which are contrary to room temperature measurements by most of the other authors as indicated in Part I (*l.c*), and are inexplicable except on grounds of large uncertain changes in the compositions. So we leave these out of our consideration.

(4) Cu^{++} ion. The doublet Γ_3 being the lowest level in the Stark-pattern for octahedrally coordinated Cu^{++} salts, we should expect them to behave similarly to the Cr^{++} and Mn^{+++} salts. But the spin moments in the two cases are one Bohr magneton against four and also the spin orbit coupling is very much larger in Cu^{++} than in Cr^{++} or Mn^{+++}. Actually, the behaviour of Cu^{++} is more resembled by the tetrahedrally coordinated Ti^{+++} or V^{+4} ion if we do not consider the differences in the spin-orbit couplings. All of the copper salts discussed here appear to obey the Curie law very well over a wide range of temperatures, except the three salts by Birch (1928) of which $CuCl_2.2H_2O$ and $CuSO_4.H_2O$ are certainly rather concentrated magnetically ; and $CuSO_4.5H_2O$ by Reekie (1939) below about 10°K, in which specific heat anomalies are also marked in this region (Ashmead, 1939) Recent measurements on the paramagnetic resonance show exchange interactions to be the cause of these anomalies (Bagguley and Griffiths 1948). The high temperature results of Birch on $CuSO_4.5H_2O$, showing a break in the $\mu_a\beta^2 - T$ curve indicates probably a change in the electric fields marked by a greater freedom for the Cu^{++} ion. There is however, a large discrepancy in the slope of the curve with those of de Haas and Gorter (Leid Comm.) and of Reekie which are certainly more reliable.

The moment curves (figure 7) for the different salts show so little difference from salt to salt that it is difficult to estimate the effects of the long range fields. This is not very strange considering the low absolute value of the effective moment in Cu^{++}, in spite of the fact that the contributions to the orbital moments are relatively fairly large.

It would be better for the above purpose to compare the three constant series representation of the results as before, *e.g.*

$$\overline{\mu_a\beta^2} - 3 = A + BT + \frac{C}{T}.$$

TABLE IV

Salt	Author	A	B	C
$CuSO_4\ H_2O$	Birch	+ 868	+.00046	−54.
$CuSO_4\ 5H_2O$	Birch (195.1–273.1°K	+ 942	+.00021	−69
	Birch (273–430°K	+1.015	+.000005	−35.
$CuCl_2.2H_2O$	do	+ 986	+.00005	−80.
$CuSO_4\ 5H_2O$	de Haas and Gorter	+.550	+.00053	− 78
$CuSO_4\ 05H_2O$	Reekie	+.651	+.00003	−1.6
$Cu(KSO_4)_2\ 6H_2O$	do	+ 6 6	+.00027	−.044
$Cu(NH_4SO_4)_2\ 6H_2O$	do	+.657	+ 00022	−.014
$Cu(KSO_4)_2\ 6H_2O$	Janes	+.558	+.0058	+4.4
$Cu(NH_4SO_4)_2\ 6H_2O$	do	+.592	+.0040	+2 5
$CuSO_4\ 4NH_3\ H_2O$	do	+.1528	+ 0009	−8.9
$Cu(KSO_4)_2.6H_2O$	Hupse	+.676	+.0035	−.051

It will be seen that the high frequency term in all the copper salts is quite negligible. It is well known that the spin-degeneracy in the 9 electron Cu^{++} ion is entirely of the Kramer's type as in Ti^{+++} or V^{++} with one electron and hence the crystalline electric field has no effect on the two-fold spin degeneracy. Thus the origin of the small C term in the various salts are either due to exchange interaction or higher order orbital contributions. Measurements of Reekie (l c.) and Hupse (Leid.Comm.) on the Tutton salts giving very small +ve values of C extend to helium temperatures and are hence more reliable than those of Janes (*l.c.*). Somewhat larger +ve values of C in Janes's measurement therefore cannot be given much significance. The most important temperature indepdendent term A, is given by the upper level contributions through the large spin-orbit coupling in Cu^{++} ion. Both Janes' and Reekie's values for the two Tutton salts agree in giving a difference in the A term in the right direction, decreasing from potassium salt to ammonium salt. The absolute values by the two authors are however somewhat different. The absolute value of A for the potassium salt by Miss Hupse is the highest of all. Again, the absolute value of the term A in $CuSO_4.5H_2O$ by Reekie is about the same as his ammonium salt, which is surprising since the pentahydrate is a triclinic crystal with no internal symmetry except inversion. Hence the orbital quenching here should have been the largest. It is to be noted that absolute value of de Haas and Corter for A term for $CuSO_4.5H_2O$ seems to give a better fit with Reekie's values for the Tutton salts, though it must be admitted that the results of the former authors being only down to 14°K give no indication of the steep downward fall in the curve below 14°K observed by Reekie. In fact, the higher value of A for $CuSO_4.5H_2O$ by Reekie might be ascribed to the inclusion of this steep part of the curve in calculating the constants of the series formula. The comparatively smaller value of A and larger −ve value of C in the salt $CuSO_4.4NH_3.H_2O$ done by Janes are no doubt owing to a much stronger field perhaps arising from a square coordination of the Cu^{++} ion with four NH_3 molecules.

The data on solutions of Cu^{++} salts are not extensive enough to enable us to compare these with the solid salts.

CONCLUSION

From the previous discussions, we have been able to show definitely that the effects of the long range electric fields on the mean effective moments in the latter half of the iron group are by no means negligible, and are particularly prominent in the Fe^{++} and Co^{++} salts. Quantitative treatment of such fields are, however, out of the question primarily owing to lack of extensive and reliable data on a large number of similarly constituted salts as also their solutions. Further, it will have to be admitted that the mean values of the moments can only give us an idea of the long range cubic field

and the averaged effect of the rhombic fields, to the variations of which the moments are not very sensitive.

The long range rhombic fields are very structure sensitive and have large influence on the magnetic anisotropies and the principal moments in the crystals. The study of these, therefore, would give us a full picture of the Jahn-Teller mechanism for asymmetrically removing the magnetic degeneracy of the paramagnetic ions. The discussion on the magnetic measurments on single crystals of these salts which alone can give us the above informations, are left for some future papers.

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